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Metal-enhancement fluorescence of silicon carbide nano-particles based on self-assembled silver films

In this paper, the fluorescence enhancement effect of silicon carbide nano-particles is studied in order to expand the application of silicon carbide nano-particles in optical and life sciences. Firstly, the luminescence mechanism, surface fluorescence enhancement and fluorescence spectrum of silicon carbide nano-materials were analyzed and metal nano-particles have enhancement effect to the surface fluorescence silicon carbide nano-materials. Then, taking silver self-assembled film metal nano-particles as an example, the preparation of silicon carbide nano-particles and silver nano-particles were performed, and the preparation methods of silver self-assembled films with different layers were described. Finally, spectral analysis of fluorescence enhancement of silicon carbide nano-particles based on silver self-assembled films was performed in an empirical manner. Through analysis, it can be seen that with the increase of the number of polyelectrolyte layers, the emission spectrum of the sample shows a trend of increasing first and then decreasing, which provides a direction for future fluorescence enhancement of silicon carbide nano-materials.

Keywords: *Silicon carbide nano-particles; silver self-assembled films; polyelectrolytes; spectral analysis; fluorescence enhancement*

1. Introduction

With the study of surface plasmon resonance and plasmon enhanced spectroscopy of precious metal nano-particles such as gold, silver and copper, surface enhancement fluorescence has received more and more attention from researchers. To use metal enhancement fluorescence mechanism to increase the luminescence intensity of silicon carbide nano-structure films can increase the practical application range of the material. In this paper, the fluorescence enhancement effect of silver nano-particles on the surface of silicon carbide nano-particles was studied in order to provide guidance for the application of silicon carbide nano-particles in the field of optics and life science.

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Many people have made efforts for the application of metal enhancement fluorescent silicon carbide nano-materials. It is these people's efforts that have laid a theoretical basis for the development of new applications for new materials. Among them: Wang Yuehui et al. (2014) studied fluorescence enhancement effect of nano silver which takes water, heavy water, ethanol and dimethylformamide as solvents and ruthenium-pyridine-2,6-dicarboxylic acid (Eu(III)DPA) as complexes solution [1]. Zhou Ting et al. (2013) used monodisperse polystyrene (PS) microspheres as raw materials and water as diluting solvent to prepare multilayer PS sphere ordered array templates using vertical sedimentation method. Sol-gel method was used to prepare TiO_2 sol and colloidal template method was used to prepare TiO_2 ordered porous films. Silver nanocrystals were then incorporated into porous membrane framework to prepare TiO_2 ordered porous luminescent film containing silver nanocrystals. The morphology and structure of silver-doped TiO_2 ordered porous film were analyzed, and fluorescence enhancement of silver-doped TiO_2 ordered porous films adsorbing Behavior Rhodamine B and fluorescent substance of quantum dot CdSe was studied [2]. Dong Jun et al. (2012) applied laser spectroscopy to study the dependence of the fluorescence enhancement effect of Rh6G molecules on copper surface and the oxide layer formed on the surface of the metal substrate, explored the effect and the mechanism of action of oxide layer formed due to the air oxidation in surface fluorescence enhancement effect. In experiments, Rhodamine 6G fluorescent probe molecules are used. Under the excitation of 532nm continuous light, mechanical polishing copper metal substrate in different oxidation time is studies and the fluorescence enhancement effect to RH6G molecules which absorb on the surface [3].

Based on previous researches, this paper researches the fluorescent enhancement effect of silicon carbide nano-materials based on silver self-assembled films in order to provide a theoretical basis for the development and application of new materials.

2. Luminescence mechanism and surface fluorescence enhancement of silicon carbide nano-materials

In semiconductors, there are two kinds of carriers, which are

electron and holes. When the heat is balanced, there are a certain number of electrons and holes in a unit volume, but under the action of the outside world, the electron concentration and hole concentration will deviate from the equilibrium value. The carries which excess thermal equilibrium are called non-equilibrium carriers.

As people continue to explore and study the atomic world, when precious metals, such as gold, silver and copper are made into nano-materials, new applications have been made in optics. The free electrons conducting in metal are no longer tied to the individual nuclei, but move throughout the system, which are common electrons. The frequency of the free electrons in metal nano-particles depends on the atomic composition, size, shape of the particles and the refractive index of the surrounding medium, and is the natural frequency of the nano-particles. When a beam of light shines on a metal nano-particle, and the frequency of entering is the same as the natural frequency of free electron oscillation of the metal nano-particle, resonance occurs, which is called surface plasmon resonance.

The thicker arrow in Fig.1 indicates increased excitation and emissivity. When a beam of light strikes the fluorophore near the metal nano-particle, the electric field will be concentrated near the metal nano-particle and plasmon resonance occurs. The enhancement of the local electric field will promote the excitation of the fluorophore near the metal nano-particle without changing the life and quantum yield of the fluorophore.

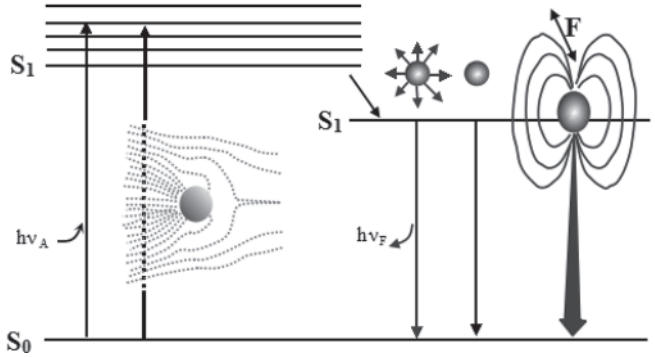

Fig.1 The luminescence mechanism of the interaction between metal and fluorophore

Another mechanism is that the excited fluorophore can generate plasmon resonance with the nearby metal nano-particles, and the plasmon in the whole system can be converted into far-field light radiation. This mechanism shortens the fluorescence lifetime and reduces the duration of the fluorescent molecule in excited state.

Unlike surface-enhancement Raman, surface-enhancement fluorescence strongly depends on the distance between the metal nano-particles and the fluorescent molecules. When the fluorescent molecules are very close to or directly adsorbed on the surface of particles, the excited molecules will transfer the energy to the metal particles and returns to the ground state through the dipole interaction. Then the fluorescence is quenched. When the two are far apart, the plasmons in the metal cannot interact with fluorescent molecules. Only when the distance is moderate, the enhancement effect is greater than the quenching effect and it will show fluorescence enhancement[4]. Therefore, controlling the interaction distance between the fluorescent molecules and the nano-particles is a key factor to obtain enhanced fluorescence. The distance between the nano-particles and the fluorescent molecules can be adjusted by using LBL polyelectrolyte assembly, multi-layer LB membrane technology, silica and various biomolecules. The regulatory distance is generally 5~20nm, where LBL polyelectrolyte assembly has the advantages of simple operation and precise adjustment with the distance within a range of 1~2nm [5]. The fluorescence phenomenon was first recorded by the Spanish physician and botanist B. Monardes in 1575, after which the phenomenon of fluorescence was extensively studied. Using fluorescence analysis methods, fluorescence was applied to industry, agriculture, life sciences, environmental sciences, materials science, food science and many other fields[6].

When the incident light irradiates the material, the electrons are excited to transition to higher energy and there are many ways to decay to the ground state. These ways are all radiative transitions. With the emission of the tube, fluorescence or phosphorescence occurs, and the radiative transition process affects luminescent properties of solids. At the same time, non-radioactive transitions, including vibrational relaxation (VR), internal transformation (ic) and intersystem crossing (isc) also occur. These decay processes cause excitation energy to be converted into heat energy for transmission to the medium. Fig.2 shows the intramolecular excitation and decay process.

Commonly used fluorescence analyzers include fluorometers and fluorescence spectrophotometers. Both analyzers include a light source, a monochromator, a slit, a sample chamber, a signal detection and amplification system, and a signal readout and recording system. The light source is used to excite the sample, the monochromator is used to separate the desired monochromatic light, the signal detection

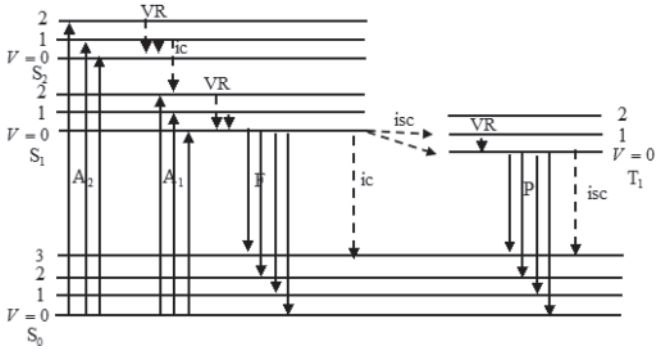

Fig.2 Intramolecular excitation and decay process

amplification system is used to convert the fluorescent signal into an electrical signal, and the readout device coupled to the amplification device is used to display the recorded fluorescent signal.

At present, ordinary fluorescent fluorophotometer adopts PMT as a detector. PMT is a very good current source. Under certain conditions, the current amount is proportional to the intensity of incident light, and it consists of a photocathode and multistage secondary emission electrode. When the light strikes the photocathode, it initiates an electron emission. These photoelectrons are accelerated by the electric field in PMT to the first secondary emitter. After many repetitions, finally the electrons are hit. The generated current is amplified to a detectable level. The role of the detector is to convert the optical signal into an electrical signal and display it.

3. Study on metal-enhanced fluorescence of silicon carbide nano-particles based on self-assembled silver films

3.1 Sample Preparation

The preparation of silicon carbide nano-particles is divided into the following three steps:

Step 1: The SiC powder is added to a 3:1 volumetric mixture of hydrofluoric acid and nitric acid.

Step 2: The mixed solution containing SiC powder is heated at 80°C for one hour.

Step 3: After heating, the supernatant of the solution of the mixture is removed and then the solution is centrifuged for five minutes. Ethanol is then added and sonicated for half an hour followed by centrifugation for ten minutes.

Then the solution is shaked with ultrasound for half an hour followed by centrifugation for ten minutes.

In the above step, the supernatant liquid is the alcohol solution of SiC nano-particles, dry the supernatant liquid and add deionized water, the preparation of SiC nano-particles can be completed.

The preparation of silver nano-particles is divided into the following two steps:

Step 1: Boil 200mL silver nitrate solution (containing 45mg silver nitrate) and 5 mL 38.8 mmol/L solution of trisodium citrate under magnetic stirring.

Step 2: The mixed solution is allowed to react for 15 minutes with stirring and boiling, and then naturally cooled to room temperature.

Under the premise of completing the above two steps, gray-black silver sol containing silver nano-particles can be obtained.

The washed silicon wafer was immersed in sulfuric acid and hydrogen peroxide solution for 30 minutes, and the volume ratio of sulfuric acid and hydrogen peroxide was 7:3. After cooling, wast it with a large amount of deionized water, and then it was immersed in 0.5 wt% PDADMAC solution. After 30 minutes, wash it with deionized water and put it into above-prepared silver sol for 12 hours. The layer-by-layer self-assembly method was used to self-assembly different layers of PAH/PSS bilayer film structures.

While maintaining the two polyelectrolyte bilayer films, 0.1, 0.5, 1, and 2 mg/mL concentrations of sodium chloride were added to PAH aqueous solution and PSS aqueous solution and the above steps were repeated to complete the deposition of polyelectrolyte films at different concentrations of sodium chloride. Structure of polyelectrolyte compounds is shown in Table 1.

Table 1 Structural formula of polyelectrolyte compound

Compounds	Abbreviation	Formulas
Poly (allylaminehydrochloride)	PAH	
Poly (styrenesulfonic acid)	PSS	
Poly (diallyldimethylammonium chloride)	PDADMAC	

Subsequently, 50μL of SiC nano-particles aqueous solution was added onto silicon wafers treated by the above two methods. After being naturally dried, SiC nanocrystalline films were obtained on silicon wafers which was used to study the enhancement fluorescence effect of SiC.

Fig.3 is a structure figure of a coupling system of SiC nano-particles separated by a PAH/PSS bilayer film and silver nano-particles. After the silicon wafer is immersed in a mixed solution of sulfuric acid and hydrogen peroxide, its surface will be negatively charged, and the silver nano-particle is also negatively charged. At this time, the polyelectrolyte PDDA with a cation is required to combine the two, namely, silver self-assemble film. Subsequently, the positive and negative polyelectrolytes PAH and PSS are layer-by-layer self-assembled to form several films, separating the silver self-assembled films and SiC nano-particles.

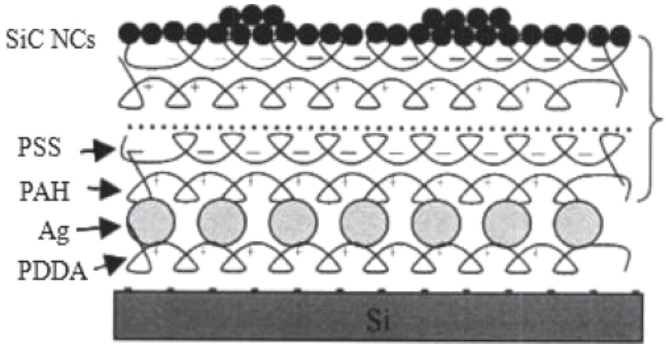

Fig.3 structure of a coupling system of SiC nanoparticles separated by a PAH/PSS bilayer film and silver nanoparticles

3.2 Spectral Analysis of Silicon Carbide Nano-particles and Silver Nano-particles

Fig.4 shows photoluminescence spectra of SiC nano-particles which is in aqueous solution and is deposited on Si wafer.

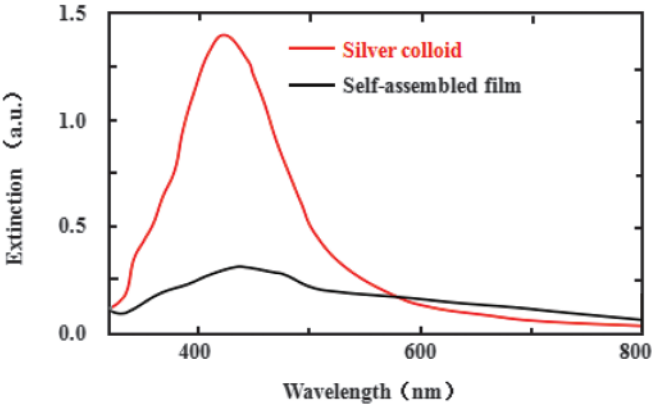

Fig.4 Photoluminescence spectra of SiC nanoparticles (left-in aqueous solution; right-deposited on Si wafer)

Through the photoluminescence spectrum shown in Fig.4, it can be seen that the spectral curve is relatively smooth and the luminous intensity is large; with the increase of the excitation wavelength, the luminous peak gradually redshifts, and the luminous intensity increases and then gradually decreases; when 420nm light is excited, the luminescence intensity is maximum. The luminescence of SiC nano-particles is a quantum confinement effect luminescence, and the luminescence is stable in an aqueous solution or an alcohol solution. The two narrow small peaks in the right figure are caused by the Raman signals of the sample.

Fig.5 shows UV visible spectrum of silver nano-particle sol and its self-assembled film. According to the analysis of the UV visible spectrum shown in Fig.5, it can be seen that the luminescence curve of silver nano-particle sol is relatively smooth, and the luminescence peak is at 426nm, which originates from the surface plasmon absorption of silver nano-particles. The red curve in the figure shows that the luminescence peak of the absorption spectrum of the self-assembled silver nano-particle film is 16nm redshifted from that in the sol; when the sol-form silver nano-particles self-assemble into the film, the refractive rate of surrounding medium will decrease from >1 to 1, then the absorption spectrum will be blue-shifted; the distance between adjacent silver nano-particles on the substrate will be much smaller than in the sol, and strong coupling will occur between the particles and make the spectrum red shift occurs, which ultimately results in a redshift of the spectrum.

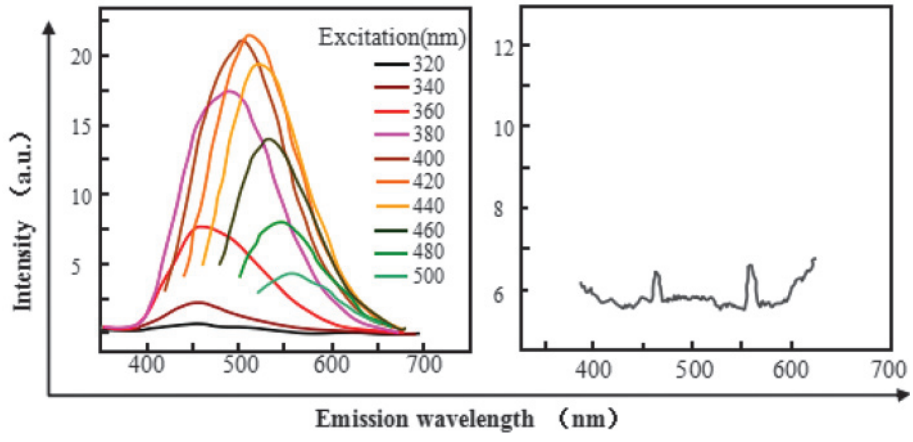

Fig.5 UV visible spectrum

3.3 Enhancement Fluorescence Spectroscopic Analysis of Silicon Carbide Nanoparticles

Photoluminescence spectra of SiC nanocrystals on silver nano-particle self-assembled films separated by two-layer PAH/PSS bilayer film and photoluminescence spectra of nanometer on silver self-assembled films under different PAH/PSS intervals with different number of layers are shown in Fig.6.

Through the photoluminescence spectrum analysis shown in Fig.6, we can see: PL spectrum curve is relatively smooth, and gradually shifts to blue with the increase of excitation photon energy, which is attributed to the quantum confinement effect and the size distribution of SiC nanocrystals. With changes of excitation wavelength, the emission peak wavelength of PL spectrum can shift as much as 30nm, which can be seen from the figure. There are two narrow small peaks in each spectrum, which are Raman spectra of polyelectrolytes PAH and PSS, and they also undergo a blue shift with the increase of excitation photon energy. The luminescence of pure SiC films is much weaker than the luminescence of SiC nano-particles in an aqueous solution, which is because during the evaporation process of aqueous solution, SiC nano-particles produce agglomeration and form micrometer-sized particles. However, when silver nano-particles are coupled with SiC nanocrystals, their luminous intensity increases.

Fig.7 shows an excitation spectrum of this sample containing four polyelectrolytes at an emission wavelength of 430nm.

By analyzing the excitation spectrum shown in Fig.7, it can be concluded that the spectrum has a smooth peak at a wavelength of 364nm which is the typical PLE peak position of SiC nanocrystals. The other part of the spectrum curve is due to the instrument's background signals.

3.4 Surface Enhancement Fluorescence at Different Sodium Chloride Concentrations

The addition of sodium chloride to polyelectrolyte solution can reduce the electrostatic repulsion between

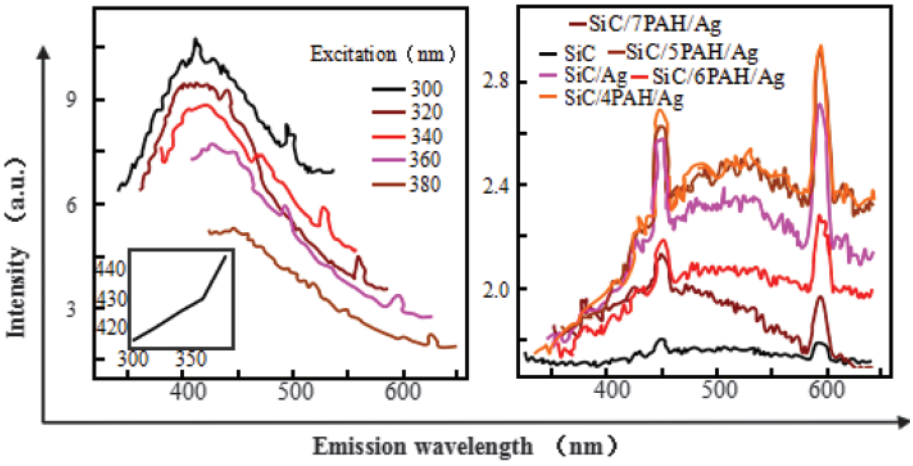

Fig.6. Photoluminescence spectra (left-layer-2 PAH/PSS; right-different-layer PAH/PSS)

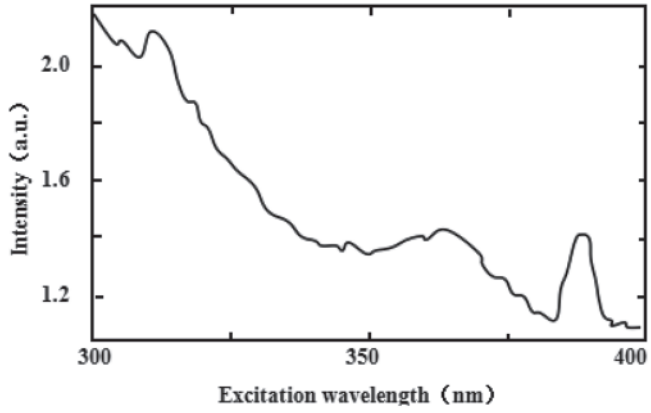

Fig.7 Excitation spectrum

polymer chains and make polymer be denser, thereby increase the thickness of each layer of polyelectrolyte. Therefore, adding sodium chloride can well debug the thickness of overall film. Fluorescence spectra of SiC quantum dots on silver self-assembled films are shown in Fig.8, where the number of layers between PAH/PSS is two.

Fig.8 shows that the number of layers of PAH/PSS bilayer films is kept as two. The distance between SiC quantum dots

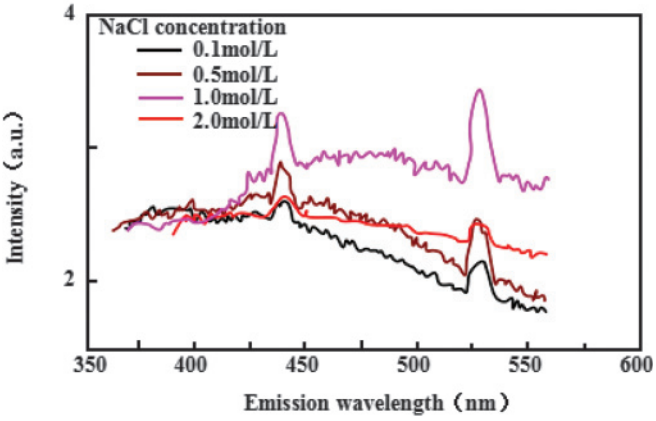

Fig.8 Fluorescence spectra of SiC quantum dots on silver self-assembled films

and Ag nano-particle thin film is adjusted by changing the concentration of NaCl in PAH/PSS polyelectrolyte solution. The two small spikes of each spectral curve are caused by Raman signals of polyelectrolytes PAH and PSS. NaCl concentration in PAH/PSS solution is 0.1 mol/L, 0.5 mol/L, 1.0 mol/L and 2.0 mol/L respectively, and their corresponding PL spectral integrated areas are shown in Fig.9.

Through the comprehensive analysis of Figs.8 and 9, it can be seen that when the concentration of NaCl is

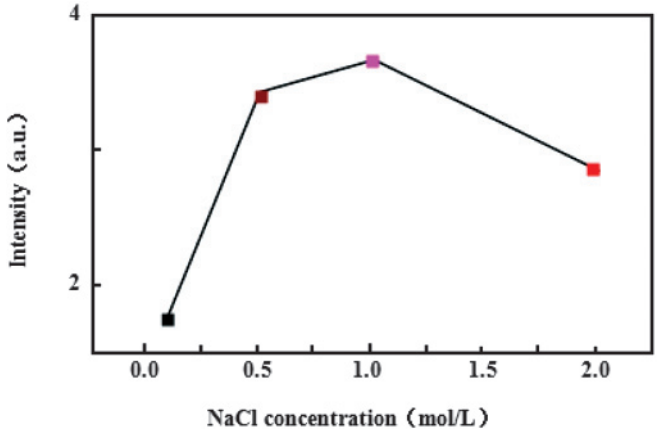

Fig.9 Schematic diagram of integral area of PL spectra corresponding to different NaCl concentrations

1.0mol/L, the luminescence intensity of SiC composite film is the largest, and when the concentration of NaCl is 0.1mol/L, the luminescence intensity is the smallest; with increase of NaCl concentration, PL spectral intensity of SiC composite film shows a trend of increasing at first and then decreasing. It is proved that metal enhancement fluorescence must satisfy the distance condition, and the enhancement intensity changes with the distance.

5. Conclusion

In this paper, based on the overview of the luminescence mechanism of SiC nano-materials, the fluorescence enhancement and the fluorescence spectroscopy analysis, the enhancement effect of metal nano-particles on surface fluorescence of SiC nano-materials was put forward. In order to explore this effect, this paper carried out research based on silicon carbide nano-particles metal enhancement fluorescence of silver self-assembled films. First of all, the preparation steps of silicon carbide nano-particles and silver nano-particle were given, focusing on silver self-assesmbled films treatment methods with different layers. Then, the

spectra of silicon carbide nano-particles and silver nano-particles were analyzed, followed by the spectral analysis of enhancement fluorescence of SiC nano-particles. Finally, the experimental results of surface enhancement fluorescence at different concentrations of sodium chloride were analyzed. With the increase of the number of polyelectrolyte layers, the emission spectrum of the sample showed a trend of increasing at first and then decreasing. The obtained spectrum had maximum enhancement of 17 times as much as that of pure SiC nano-crystal films. The strong coupling between luminescence of SiC nano-crystals and surface plasma oscillation of silver nano-particles is the main reason for the enhancement of luminescence spectra.

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